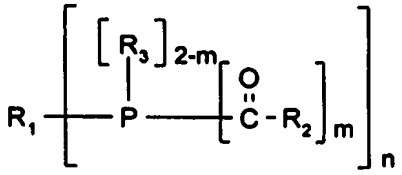
Claims

1. A process for the preparation of acylphosphanes of formula I



(I), wherein

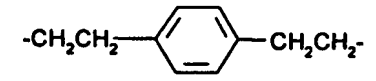
n and m are each independently of the other 1 or 2;

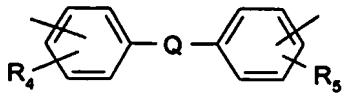
R_1, if n = 1, is

C_1-C_{18}alkyl, C_2-C_{18}alkyl which is interrupted by one or several non-successive O atoms; phenyl-C_1-C_4alkyl, C_2-C_8alkenyl, phenyl, naphthyl, biphenyl, C_5-C_{12}cycloalkyl or a 5- or 6-membered O-, S- or N-containing heterocyclic ring, the radicals phenyl, naphthyl, biphenyl, C_5-C_{12}cycloalkyl or the 5- or 6-membered O-, S- or N-containing heterocyclic ring being unsubstituted or substituted by one to five halogen, C_1-C_8alkyl, C_1-C_8alkylthio, C_1-C_8alkoxy and/or $-N(R_8)_2$;

R_1, if n = 2, is

C_1-C_{18}alkylene, C_2-C_{18}alkylene which is interrupted by one or several non-successive O atoms; or R_1 is C_1-C_8alkylene which is substituted by C_1-C_4alkoxy, phenyl, C_1-C_4alkyl-phenyl, phenyl-C_1-C_4alkyl or C_1-C_8alkoxyphenyl; or R_1 is phenylene or xylylene, which radicals are unsubstituted or substituted by one to three C_1-C_4alkyl and/or C_1-C_4alkoxy, or

R_1 is a $-CH_2CH{=}CHCH_2-$, $-CH_2-C{\equiv}C-CH_2-$,  ,

 or  group;

R_2 is C_1-C_{18}alkyl, C_3-C_{12}cycloalkyl, C_2-C_{18}alkenyl, phenyl-C_1-C_4alkyl, phenyl, naphthyl, biphenyl or a 5- or 6-membered O-, S- or N-containing heterocyclic ring, the radicals phenyl, naphthyl, biphenyl or the 5- or 6-membered O-, S- or N-containing heterocyclic ring being unsubstituted or substituted by one to five halogen, C_1-C_8alkyl, C_1-C_8alkoxy and/or C_1-C_8alkylthio;

R_3 is C_1-C_{18}alkyl, C_2-C_{18}alkyl which is interrupted by one or several non-successive O atoms or which is interrupted by –CO-, –COO-, -OCO-, -OCOO-, -CO-N(R_9)-, -N(R_9)-CO-,

-N(R_9)-CO-N(R_9)-, -N(R_9)-COO-; C_1-C_{18} alkyl substituted by –OR_{10}, -OCO-R_{10}, -COO-R_{10}, -N(R_9)-CO-R_{10}, -CO-N(R_9)-R_{10}, -C(R_{11})=C(R_{12})-CO-OR_{10} or -C(R_{11})=C(R_{12})-phenyl;

C_2-C_{12}alkenyl or C_2-C_{12}alkenyl which is interrupted by one or several non-successive O atoms; phenyl-C_1-C_4alkyl, phenyl, naphthyl, biphenyl, C_5-C_{12}cycloalkyl or a 5- or 6-membered O-, S- or N-containing heterocyclic ring, the radicals phenyl, naphthyl, biphenyl, C_5-C_{12}cycloalkyl or the 5- or 6-membered O-, S- or N-containing heterocyclic ring being unsubstituted or substituted by one to five halogen, C_1-C_8alkyl, C_1-C_8alkylthio C_1-C_8alkoxy and/or –N(R_8)$_2$; or R_3 is –CO-OR_9 or –CO-N(R_9)$_2$;

Q is a single bond, CR_6R_7, -O- or -S- ;

R_4 and R_5 are each independently of the other hydrogen, C_1-C_4alkyl or C_1-C_4alkoxy;

R_6 and R_7 are each independently of the other hydrogen or C_1-C_4alkyl;

R_8 is C_1-C_{18} alkyl, C_2-C_{18} alkyl which is interrupted by one or several non-successive O-atoms; or -N(R_8)$_2$ forms a 5- or 6-membered O-, S- or N-containing heterocyclic ring;

R_9 is hydrogen, C_1-C_{18}alkyl, C_2-C_{18}alkyl which is interrupted by one or several non-successive O atoms, C_3-C_{12}-cycloalkyl, C_2-C_{18}-alkenyl, phenyl-C_1-C_4-alkyl, phenyl, naphthyl, pyridyl, the radicals phenyl, naphthyl or pyridyl being unsubstituted or substituted by one to five C_1-C_8-alkyl, C_1-C_8-alkoxy, C_1-C_8-alkylthio and/or halogen; or -N(R_9)$_2$ forms a 5- or 6-membered O-, S- or N-containing heterocyclic ring;

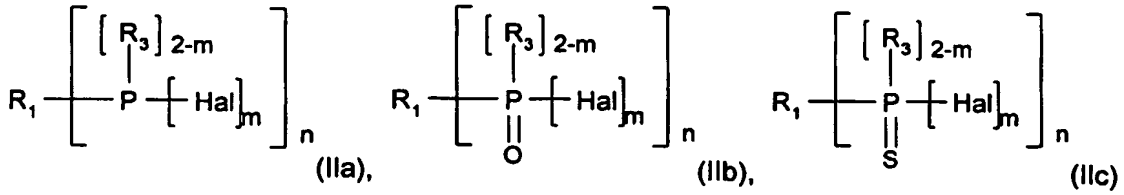
R_{10} is C_1-C_{18}alkyl, C_2-C_{18}alkyl which is interrupted by one or several non-successive O-atoms, C_3-C_{12}-cycloalkyl, phenyl-C_1-C_4-alkyl, C_2-C_{18}-alkenyl, phenyl, naphthyl, biphenyl; the radicals phenyl-C_1-C_4-alkyl, phenyl, naphthyl or biphenyl being unsubstituted or substituted by one to five C_1-C_8-alkyl, C_1-C_8-alkoxy, C_1-C_8-alkylthio and/or halogen;

R_{11} is hydrogen or C_1-C_4-alkyl;

R_{12} is hydrogen or C_1-C_4-alkyl;

by

(1) reacting a phosphorous halide of formula IIa or a phosphorous halide oxide of formula IIb or a phosphorous halide sulfide of formula IIc



(IIa), (IIb), (IIc)

wherein R_1, R_3, n and m have the meaning cited above and Hal is F, Cl, Br or I;

with an alkali metal in a solvent **(metallation)** in the presence of a proton source **(reduction)**;

(2) subsequent reaction with m acid halides of formula III

(III),

wherein R_2, Hal and m have the meaning cited above.

2. A process according to claim 1, wherein in step (1) the metallation is carried out by reacting a compound of the formula IIa, IIb, or IIc with an alkali metal in a solvent, whereby a metallized phosphanide of the formula V

$$R_1\text{-}P(Me)\text{-}P(Me)\text{-}R_1 \quad (V)$$

is formed together with cyclic phosphanes $(R_1P)_n$, $n \geq 3$ as intermediates, wherein
Me is lithium, sodium or potassium or magnesium in combination with lithium, and
R_1 is as defined in claim 1; and
wherein the reduction is carried out by reacting the intermediate V and/or $(R_1P)_n$, $n \geq 3$ with a proton source.

3. A process according to claim 2, wherein
the alkali metal is sodium;
the proton source is selected from sterically hindered alcohols, trialkylamine hydrohalogenes, bisarylamines, malono nitrile, malonic acid esters, amidine hydrohalogene and carboxylic acids;
the solvent is benzene, toluene, o-, m- or p-xylene, mesitylene, ethylbenzene, diphenylethane, 1,2,3,4-tetrahydronaphthaline (tetraline), isopropylbenzene (cumol) and mixtures thereof; and
the reaction temperature of step (1) is in the range from -20°C to +160°C.

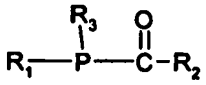
4. A process according to claim 3, wherein the sterically hindered alcohol is selected from the group consisting of secondary or tertiary C_3-C_{18}alcohols, preferably of t-butanol, tert.-amyl-alcohol, 3-methyl-3-pentanol, 3-ethyl-3-pentanol, triphenylmethanol, 3,7-dimethyl-3-octanol, 2-methyl-1-phenyl-2-propanol, 2-methyl-4-phenyl-2-butanol, fenchyl alcohol, 2,4-dimethyl-3-pentanol, 1-dimethylamino-2-propanol or hexylene glycol.

5. A process according to any one of claims 1-3, wherein the metallation is carried out in the presence of catalytic amounts of alkali or earth alkali hydroxides or of Na, K or Li alcoholates or of alcohols, preferably sterically hindered alcoholates or alcohols.

6. A process according to any one of claims 1-3, wherein the metallation and reduction step is carried out in the presence of an activator.

7. A process according to claim 6, wherein the activator is an amine selected from triethylamine, tributylamine, piperidine, morpholine, N-methylpiperidine, N-methyl morpholine or a polyamine such as N,N,N',N'-tetramethylethylenediamine (TMEDA).

8. A process according to claim 1 for the preparation of **monoacylphosphanes** of the formula I'

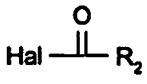

(I') by

(1) reacting organic phosphorus halides of formula II'

R_1-P(Hal)$_2$ (II')

with an alkali metal in a solvent in the presence of a proton source;

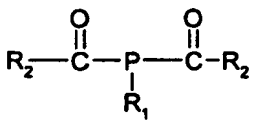
(2) subsequent reaction with an acid halide of formula III'



followed by the reaction with an electrophilic compound R_3-Hal or vice versa,

wherein R_1, R_2 and R_3 and Hal are as defined in claim 1.

9. A process according to claim 1 for the preparation of **symmetric bisacylphosphanes** of the formula I" (compounds of the formula I with n=1 and m=2)

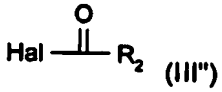

(I"), by

(1) reacting organic phosphorus halides of formula II"

R_1-P(Hal)$_2$ (II")

with an alkali metal in a solvent in the presence of a proton source;

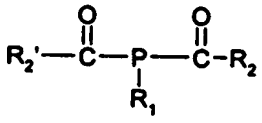
(2) subsequent reaction with an acid halide of formula III"



(III")

wherein R_1 and R_2 and Hal are as defined in claim 1.

10. A process according to claim 1 for the preparation of **unsymmetric bisacylphosphanes** of the formula I'''



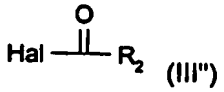
(I''') by

(1) reacting organic phosphorus halides of formula II"

R_1-P(Hal)$_2$ (II")

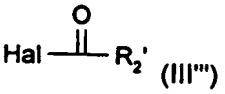
with an alkali metal in a solvent in the presence of a proton source;

(2) subsequent reaction with an acid halide of formula III"



(III")

(3) subsequent reaction with a second acid halide III'''



(III''')

wherein

R_1 is as defined in claim 1 and

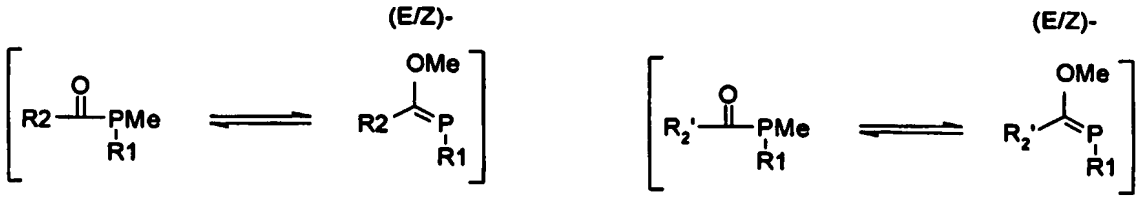
R_2 and R_2' independently of one another are as defined in claim 1 under R_2 with the proviso that R_2 is not equal R_2',

Hal is as defined in claim 1.

11. A process according to claim 1, wherein step (1) is carried out by reacting diphospanes of the formula $(R_1)_2$-P-P$(R_1)_2$ or polyphosphanes of the formula [R_1P]n, wherein R_1 is as defined above and n is ≥ 3, with an alkali metal in a solvent in the presence of a proton

source; followed by the reaction with acid halides (III, III', III", III'") and/or by reaction with electrophilic compounds R_3-Hal.

12. A process for the preparation of mono acylated phosphanes of the formula VI and VI'



VI VI'

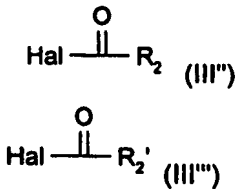
by

(1) reacting organic phosphorus halides of formula II"

$$R_1\text{-}P(Hal)_2 \quad (II")$$

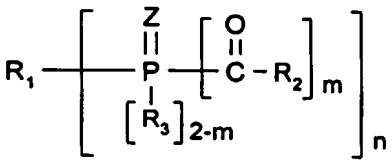
with an alkali metal in a solvent in the presence of a proton source;

(2) subsequent reaction with an acid halide of formula III" or III'"



wherein R_1, R_2 are as defined in claim 1 R_2' is as defined in claim 10 and Me is Li, Na, K or Mg in combination with Li.

13. A process for the preparation of acylphosphane oxides and acylphosphane sulfides of formula IV



(IV), wherein

R_1, R_2, R_3, n and m are as defined in claim1 , and Z is O or S,

by oxidation or reaction with sulfur of the acylphosphane of formula I, I', I" or I'"

as defined in claims 1,8,9 and 10.